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UNILEVER PLC

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(57) Claim

1. A liquid cleaning composition characterised in that it comprises 3 to 50wt% of a water-insoluble solid having an average particle size not greater than 100 μ , suspended in an aqueous solution or emulsion comprising 30 to 90wt% water and 0.05 to 5wt% surfactant, with all percentages being based on the whole composition, characterised in that the ratio of the specific surface area of insoluble solid to the weight of those constituents of the composition which are involatile liquid and semi-liquids which do not boil at temperatures less than 220°C is at least 50 and not greater than 200 square metres per gram of these involatiles.

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(57) Abstract			
<p>A liquid cleaning composition comprises 3 to 50 wt% water-insoluble solid having an average particle size not greater than 100 μ, suspended in an aqueous solution or emulsion comprising 30 to 90 wt% water and 0.05 to 5 wt% surfactant, with all percentages being based on the whole composition, the ratio of the specific surface area of insoluble solid to the weight of those constituents of the composition which are involatile liquid and semi-liquids which do not boil at temperatures less than 220°C is at least 50 and not more than 200 square metres per gram of these involatiles. The composition is suitable for cleaning hard surfaces in either a dry or a wet use. Compliance with the stated ratio limit leads to improved cleaning results.</p>			

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CLEANING COMPOSITION

Technical Field

This invention relates to cleaning compositions suitable for use on hard surfaces such as glass, plastic laminates and ceramic tiles. The compositions to which the invention relates are liquid cleaning compositions containing a finely divided water-insoluble solid suspended in an aqueous solution or emulsion which generally contains a low level of surfactant.

Background Art

A wide variety of liquid abrasive cleaners have been proposed in the past. Many of the proposals have claimed to overcome specific problems. For example, GB 2 125 428 (Unilever PLC) describes a liquid scouring cleanser composition comprising a suspending liquid medium, a detergent surfactant and an abrasive powder having a mean particle size of between 4 and 17.5 microns and containing substantially no particles with sizes above 75 microns. Attention to such low mean particle size abrasive is said to provide a product which does not produce visible

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scratching, has good rinse-away properties and does not feel gritty. GB 2 031 455 (Colgate-Palmolive Company) is concerned with liquid cleaning compositions suitable for cleaning hard surfaces, containing 1 to 20% water-insoluble particulate inorganic abrasive having a particle size in the range 1 to 40 microns, 3 to 15% water soluble synthetic, organic, anionic detergent, from 1 to 7.5% water-soluble, alkyleneoxylated C_8-C_{22} alkanol nonionic detergent, from 1 to 15% water soluble builder salt comprising 1 to 3 wt% alkali metal silicate having an alkali metal oxide to silicon dioxide ratio of 1:1.5 to 1:4, the weight ratio of builder to total detergent being in the range 1:4 to 2:1, and an aqueous medium, the proportions of the components being so adjusted within the specified ranges that some of the detergent is present in liquid crystal form and the abrasive is maintained in stable suspension. The liquid crystal form of the detergent is said to increase the viscosity of the composition which it is said may be responsible for hindering the abrasive particles from setting out and hence remain stably suspended. EP-A- 0 050 887 (Unilever PLC) pertains to liquid media, in which particulate materials can be stably suspended e.g. liquid abrasive cleaning compositions. Stability of the suspended undissolved particulate material, particularly against breakdown at high extensional shear rates such as might be experienced during manufacture, can it is reported be improved by inclusion in the liquid suspending medium of 0.001 to 0.2wt% of a hectorite clay.

Disclosure of the Invention

The present invention is concerned with compositions which are intended to be spread onto the surface to be cleaned which is then rubbed with an absorbent and

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preferably dry material, e.g. a cloth or a paper wipe. The suspended solid functions in two ways. Firstly it functions as an abrasive: in this regard the solid may be chosen to be only a mild abrasive in order to be suitable for use on plastic surfaces. Secondly, after evaporation of water and any other volatiles, the solid functions as a "soil-sink" by providing surface area to take up soil mobilised from the surface being cleaned together with some of the involatile liquid constituents of the composition. The solid, together with this mobilised soil and involatile liquid from the composition can be picked up by a dry cloth, paper wipe or other absorbent material and thus removed from the surface being cleaned. Alternatively, the solid and material absorbed thereon may be rinsed away with a stream of water or a wet cloth.

We have found that in such a composition it is advantageous to have a ratio of the insoluble solid to other constituents which is defined by reference to the surface area provided by the insoluble solid.

Accordingly the present invention provides a liquid cleaning composition comprising 3 to 50% of a water-insoluble solid having an average particle size not greater than 100μ , suspended in an aqueous solution or emulsion comprising 30 to 90% water and 0.05 to 5% surfactant, with all percentages being based on the whole composition, characterised in that the ratio of specific surface area of insoluble solid to the weight of those constituents of the composition which are involatile liquid and semi-liquids which do not boil at temperatures less than 220°C is at least 50 and not greater than 200 square metres per gram of these involatiles. Preferably the ratio lies in a range from 50 up to 150 square metres per gram.

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These involatile liquid or semi-liquid constituents which do not boil at less than 220°C remain as a liquid film on the surface which is being cleaned after the more volatile constituents, including water, evaporate. The present involatile constituents which do not boil at less than 220°C, by which we mean in a pure state, can be further defined with regard to their Evaporation Rate. The presently defined involatile liquid or semi-liquid constituents suitably also have an evaporation rate of ≤ 0.01 relative to n-butyl acetate as standard of 1. By "semi-liquid" we include for example liquids that in use undergo liquid crystalline phase formation.

If the insoluble solid provides less than 50m² of surface area per gram of involatiles, we have found there is a risk that the composition may leave streaks on the surface being cleaned. The present composition can thus provide a liquid cleaning composition that can be easier to use and/or in use gives a better finish.

If the surface area is greater than 200m² per gram of involatiles, there is a risk that the insoluble solid removed from the surface onto the cloth or paper wipe will remain dusty and be objectionable to the user because of this dustiness.

A strongly preferred feature is that the ratio of the specific surface area of the insoluble solid to soluble electrolyte (if any) in the composition is such that the insoluble solid provides at least 40 square metres of surface area per gram of dissolved electrolyte (if any).

If the amount of surface area provided by the insoluble solid is less than 40m² per gram of soluble electrolyte, there is a possibility that when the

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composition is spread on a surface, the crystallisation of the soluble electrolyte which takes place as water evaporates will cement the insoluble solid particles together.

5

Compositions of this invention have been found in use to give a finish to cleaned surfaces which is of an exceptionally bright appearance. When the surface which has been cleaned is glass, the presence of a very thin residual film of involatile ingredient can be demonstrated by breathing on the clean, cold surface. Interference patterns (e.g. Newton's rings) in the resulting thin continuous film are visible under certain conditions of lighting. This demonstrates that anti-misting properties are being provided. It is believed that this exceptionally bright appearance arises through deposition of a particularly thin residual film on the clean surface.

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The compositions of this invention require to be able to retain the insoluble solid in suspension, yet be capable of being spread on the surface to be cleaned. These characteristics are antagonistic. In order to achieve both it is necessary that the composition is strongly shear thinning.

30

In order that the solution or emulsion should be able to suspend the solid constituents of the composition and yet provide a sprayable composition it is strongly preferred to include a polymeric thickener at a low level, up to 3.5% by weight, preferably between 0.01 and 1.0wt%, more preferably between 0.01 and 0.8wt%, even more and preferably 0.01% to 0.2% by weight.

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Such use of a low level of thickener can provide a very strong shear thinning characteristic, facilitating

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the suspension of solid but also enabling it to be distributed easily. A composition of this invention generally should have a viscosity of not more than 60 centipoise at a 1000sec^{-1} shear rate, preferably not more than 30 centipoise at this shear rate.

The compositions of this invention may be applied to a surface by pouring some of the composition onto a cloth or some other kind of wiping article and then wiping this over the surface. An alternative is for the composition to be delivered by spraying. The invention therefore extends to a composition as stated above, packed in a portable container provided with a pump for discharging the composition from the container as a spray.

Constituents classing as involatiles include the surfactant and at least part of any perfume which is included in the composition. As a working approximation, about half of a conventional perfume will boil above 220°C .

Another preferred feature for compositions of this invention is for the solution or emulsion to contain from 0.2 to 20wt% of organic solvent, preferably from 2 to 20wt% of organic solvent, to assist in mobilising soils from the surface to be cleaned. The organic solvent employed may comprise a mixture of components. The solvent is preferably volatile, e.g. with a boiling point not over 220°C at atmospheric pressure of 760mm Hg. More preferably the solvent is present at a level of 5 to 15 wt% with respect to the total composition. It may be wholly or partially miscible with water as in the case of isopropanol or butanol, or it may be a paraffinic solvent, immiscible with water. A mixture of paraffins having a boiling point of between 170 and 220°C is suitable. For

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solvents other than hydrocarbons it is preferred that their boiling point is not over 190°C at atmospheric pressure.

5 It is preferred that the solvent and thickener should both be present, so preferred forms of the invention, utilising a combination of features, have the said 3 to 50% of insoluble solid suspended in an emulsion or solution containing:

10 30 to 90% of water

0.05 preferably 0.1 up to 5% of surfactant

0.01 to 3.5% of polymeric thickener

15 3 to 20% of organic solvent.

Preferred compositions with substantial levels of solid phase, suspended in a strongly shear thinning emulsion, contain 10 to 50% of solid and 5 to 20% of paraffinic solvent, more preferred compositions contain 10 to 40% of solid and 10 to 20% of paraffinic solvent.

20 In such forms of the invention there are three phases present, namely insoluble solid, aqueous solution which is the continuous phase of the emulsion and thirdly paraffin which is the disperse phase of the emulsion. Other forms of the invention have only two phases, i.e. no separate organic liquid phase.

25 Both when there are three phases present and when only two phases are present, the aqueous solution may (as already indicated) contain some dissolved inorganic salts. Such salts may serve to buffer the aqueous solution to an alkaline pH, which enhances the cleaning efficiency of the aqueous phase. The presence of between 0.05 and 2.5% by weight of soluble salt(s) can be used in controlling

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viscosity and shear thinning behaviour. Carbonate, bicarbonate and sesquicarbonate are preferred. Other suitable salts include sulphates.

5 The materials used in the present compositions are further discussed below.

Insoluble solid

10 The preferred particle size range of the insoluble solid will differ according to whether the composition is intended to be sprayable or not.

15 For all compositions of this invention it is desirable that a substantial proportion of the insoluble solid is of small particle size, not larger than 10μ . Small particles contribute large specific surface area; they serve to effect polishing and mild abrasion as the surface is rubbed with a cloth and they absorb liquid constituents of the composition along with soil freed from the surface being cleaned.

20 For a sprayable composition, where there is need to pass through a spray nozzle, it is very desirable that 90% of the insoluble solid particles have a size less than 10μ , while any remainder are not very much larger than this, so that 99% of the insoluble solid has a particle size less than 15μ .

30 If a composition is not intended to be sprayable it is possible to include some insoluble solid with particle sizes in the range from 10 to 100μ . Such larger particles will give a greater abrasive action and may be included where this is desired.

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The amount of particles having a size in the range from 10 to 15 μ up to 100 μ may then be up to 20% by weight based on the whole composition, e.g. 1 to 20% by weight. The amount of particles smaller than 10 μ will then be such that the total quantity of insoluble solid lies in the range from 3 to 50% by weight based on the whole composition.

Whether the composition is sprayable or not, the insoluble solid which is incorporated will generally be an inorganic mineral. A preferred mineral is calcite which, at particle sizes below about 10 μ , is a relatively mild abrasive. Other materials which are harder and therefore represent harsher abrasives may also be use. Possibilities are amorphous silica, feldspar and dolomite. Possible softer abrasives giving an even milder action are gypsum and kaolin.

As regards the material with particle size of less than 10 μ , the average particle size is preferably less than 5 μ . The specific area of the solid mineral with particle size less than 10 μ should be at least one square metre per gram and preferably lies in a range from 1m²g⁻¹ to 7m²g⁻¹. A specific surface area greater than 10 square metres per gram is possible and could be used, but it is generally not necessary to do so. Highly porous minerals, such as diatomaceous earth and high surface area calcites obtained by precipitation of calcium carbonate, lack mechanical strength and for this reason are not preferred.

Specific surface areas of solid minerals can be determined by the standard Brunauer, Emmet and Teller (BET) method, using for example a Quantasorb machine form Quantachrome Corporation. It has been found convenient to employ forms of calcite made by grinding calcium carbonate

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rock to a sufficiently small particle size that the specific surface area lies in a range from $0.5\text{m}^2\text{g}^{-1}$ to $8\text{m}^2\text{g}^{-1}$, more suitably $2\text{m}^2\text{g}^{-1}$ to $8\text{m}^2\text{g}^{-1}$.

5 Surfactant

Surfactant which is employed should be such that in use, when the volatile materials of the liquid phase evaporate, the surfactant remains as part of a liquid
10 film. One or a mixture of surfactants may be employed. It is possible to use or include some anionic surfactants, e.g. those which form a concentrated liquid phase. Possibilities are sodium C_{10-12} alkyl benzene sulphonates, sodium C_{12-15} synthetic alcohol 3EO sulphates and sodium
15 C_{12-14} primary alkyl sulphonates (i.e. coco PAS). C_{10-16} secondary alkyl sulphonates are further possibilities. There is advantage, however, in using a surfactant which even when anhydrous is liquid at room temperature. Many
20 nonionic surfactants are liquids at room temperature with boiling points in excess of 220°C and for this reason nonionic surfactants are preferred.

The nonionic surfactant which is used may in particular be one or more compounds produced by the
25 condensation of alkylene oxide groups i.e. be nonionic ethoxylate, which are hydrophilic in nature, with an organic hydrophobic compound which may be aliphatic or alkyl aromatic in nature. The length of the hydrophilic
30 or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. Particular examples include the condensation product of
35 aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with

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ethylene oxid , such as a coconut oil ethylene oxide condensate having from 2 to 15 moles of ethylene oxide per mole of coconut alcohol, and condensates of synthetic primary or secondary alcohols having 8 to 15 carbon atoms with 3 to 12 moles of ethylene oxide per mole of the synthetic alcohol; condensates of alkylphenols whose alkyl group contains from 6 to 12 carbon atoms with 5 to 25 moles of ethylene oxide per mole of alkylphenol; condensates of the reaction product of ethylenediamine and propylene oxide with ethylene oxide, the condensates containing from 40 to 80% of polyoxyethylene radicals by weight and having a molecular weight of from 5,000 to 11,000; block copolymers of ethylene oxide and propylene oxide; tertiary amine oxides of structure R_3NO , where one group R is an alkyl group of 8 to 18 carbon atoms and the others are each methyl, ethyl or hydroxyethyl groups, for instance dimethyldodecylamine oxide; glycosides or polyglycosides etherified with at least one C_8-C_{22} alkyl group or esterified with at least one C_8-C_{22} fatty acyl group; fatty acid alkylolamides; and alkylene oxide condensates of fatty acid alkylolamides.

Mixtures of two or more of nonionic detergent actives can be employed in the detergent composition of the invention. It is preferred to use at least 0.1% surfactant.

Organic Solvents

Suitable solvents which are immiscible with water include paraffinic and olefinic hydrocarbons boiling in the range 170 to 220°C and alkyl benzenes boiling in the range 150 to 190°C. Particular examples include n-paraffins such as decane, dodecane and mixtures thereof - suitable commercially available materials are Exxsol D50

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and D60 (ex Exxon); isoparaffins such as commercial mixtures sold as Shellsol T (ex Shell) and Isopars L, H (ex Exxon) and alpha-olefins such as 1-decene and 1-dodecene. All of the above suitably have boiling points from 170 to 220°C. Also suitable are alkyl benzenes such as n- and iso- C₄ to C₆ alkyl benzenes which have boiling points from 160 to 220°C.

Suitable at least partially water-soluble solvents include C₂ to C₆, preferably C₂ to C₄, aliphatic alcohols and C₂ to C₄ glycol monoethers with C₂ to C₆, preferably C₂ to C₄, aliphatic alcohols. Particular examples include ethanol, isopropanol, n-propanol, n-butanol and the propylene glycol and ethylene glycol mono ethers of C₂-C₄ aliphatic alcohols.

Polymeric Thickeners

Suitable polymeric thickeners are water soluble or at least water dispersible, and capable of thickening when incorporated at low levels, thus giving economy and shear thinning characteristics. The polymeric thickener is preferably, but need not be, electrolyte tolerant. Preferred is xanthan gum which may be used at levels ranging from 0.01% to 0.2% by weight based on the composition as a whole although higher levels are also possible up to for example 1.0wt% or of 0.8% by weight mentioned earlier. Other possible polymers are anionic polyacrylates. Desirable usage levels for these are higher, e.g. from 0.03% to 0.5% by weight and possibly up to 0.8% by weight or 1.0% by weight. Modified starches can also be used up to about 3.5wt%.

We have found that an advantageous thickener system for use in the present compositions comprises a thickening

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5 mixture comprising either a gum type polymer and an
acrylic-type polymer or a linear non-starch type polymer
and a branched starch type polymer, wherein each of the
said polymers is selected according to its respective
sigmoid curve of \log (viscosity) vs \log (concentration) as
measured in the present composition, each polymer being
selected from its sigmoid curve's lower portion having an
increasing or substantially constant gradient, such that
10 the thickened composition has a viscosity of at least 20
cPs at a shear rate of 10 sec^{-1} greater than that of the
composition in the absence of the said thickening mixture.

15 It has been found that in liquid compositions so
formulated a synergistic thickening effect can be achieved
together with shear-thinning, thus providing good flow
properties. The synergistic thickening mixture can
contain more than one of each of the two types of
thickening agent.

20 It is well known in the field of organic, polymeric
thickening agents that, in general, the viscosity (η) of
a liquid is dependent on the concentration of thickening
agent in that liquid. This relationship can be expressed
schematically as a sigmoid curve as shown in Figure 1
25 which is a plot of $\log \eta$ vs $\log c$ for the thickening agent
in the given liquid. While not wishing to be bound by
any theory, we believe that in region A the molecules are
essentially independent of one another, the viscosity
increase arises from disruption of flow of the continuous
30 phase, and the rate of increase is relatively small. In
region B the molecules are sufficiently close together to
interact, entangle etc., and the viscosity rises very
steeply. In region C the units are close packed and
35 increasingly experience compression so that once again the
rate of increase in viscosity is relatively small.

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Region A is defined as that portion of the sigmoid curve where the viscosity of the total system corresponds approximately to that of the base system and there is a linear relationship between $\log \eta$ and $\log c$.

Region B (lower) is defined as that portion of the sigmoid curve which obeys a power law relationship (the coefficient of which is greater than 1) beneath the point of inflexion.

Region B (upper) is defined as that portion of the sigmoid curve which obeys a power law relationship (the coefficient of which is greater than 1) above the point of inflexion.

Region C is defined as that portion of the sigmoid curve where the viscosity of the total system is greater than that of the base system and there is an essentially linear relationship between $\log \eta$ and $\log c$.

The point of inflexion for the sigmoid curve is defined as that point where the first derivative of the curve experiences a turning point.

For a given liquid system the position of the sigmoid curve on the $\log \eta$ vs $\log c$ graph will depend on, for example, polymer type or temperature. It is therefore convenient to describe a given system in terms of a single master curve which represents the actual measured parameter plus a shift factor which superposes the measured curve on the reference curve.

Reference sigmoid curves can be constructed according to the method described in R Simha and L Utracki, J Polymer Sci, A-2, 5, 853 (1967), L Utracki and R Simha, J

Polymer Sci, A, I, 1089 (1963) and R Simha and L Utracki, Rheol. Acta, 12, 455 (1973). For a liquid system comprising a gum-type polymer and for a liquid system comprising an acrylic-type polymer typical sigmoid curves
5 are shown in Figures 2 and 3, which are respectively plots of $\log \eta$ vs $\log c$ for Jaguar HP60, which is a cellulose derived polymer, and PPE1042 which is a cross-linked acrylic polymer.

10 In the ideal case the sigmoid curve for each polymer will be as shown in Figure 1. The lower portion of the curve from which the present preferred polymers should be selected thus corresponds in the ideal case to region A
15 and region B (lower), subject to the limitation that sufficient polymers must be present to effect an increase in the system of at least 20 cPs at a shear rate of 10 sec^{-1} . In practice when the present curves are constructed for a variety of polymers not all polymers
20 follow an ideal sigmoid curve. An overall sigmoid shape can be discerned allowing the presently defined lower portion to be identified i.e. that portion having a constant or increasing gradient and extending between a point near the origin along the curve until the gradient
25 begins to decrease. In some instances however region C may in effect be non-existent as the viscosity at such concentrations may be too high to measure readily or alternatively region C may include a second point of inflexion. In the latter instance it is only the lower
30 portion of the curve up until the first point of inflexion from which the polymer should be selected. Another non-ideal variant in the shape of the sigmoid curve may include a region of substantially constant gradient
35 between region B (lower) and region B (upper). Such region would fall within the present definition of the lower portion of the curve from which the present polymers

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must be selected. It should be noted that the sigmoid curves to be employed are those measured according to the present compositions, i.e. the compositions containing at least surfactant, and water-insoluble solid.

5

Preferably the relative weight ratio between the gum-type and the acrylic copolymer-type thickening agent, or between the linear non-starch type polymer and the branched starch type polymer, in the thickening mixture ranges from 50:1 to 1:100, preferably from 20:1 to 1:25 and more preferably from 5:1 to 1:10.

10

Examples of gum-type thickening agent, which are generally gums or mucilages basically consisting of polysaccharides with varying polymerization degrees, include the polysaccharide hydrocolloids, which are usually prepared from gums, and they may have been chemically modified, e.g. by partial acetylation, to make them more water-soluble and/or stable in the presence of the other ingredients in the liquid media. Biopolymers also belonging to this class of polysaccharide hydrocolloids are known thickening agents. Typical examples of commercially available, gum-type thickening agents are xanthan gums and their derivatives. These include a partially acetylated xanthan gum, "Kelzan" ex Kelco Company of N.J., USA, Shellflo-XA and Enorflo-XA, xanthan gums ex Shell Chemicals Ltd., and Rhodapol, a xanthan gum ex Rhone-Poulenc SA. A further example is the biopolymer Shellflo S, a succinoglucan ex Shell Chemicals Ltd. Yet other gum-type thickening agents are those derived from guar gums, such as the Jaguar(R) products ex Stein, Hall and Co Inc. and those derived from cellulose such as carboxymethyl or hydroxyethyl cellulose.

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Examples of acrylic-type polymer thickening agents include acrylat homo- or copolymers and derivatives thereof. Typical examples of such materials which are suitably cross-linked are the acrylic copolymers sold by National Starch and Chemical Ltd under the trade names EP 1910 and PPE 1042. Other types of such (meth)acrylic homo- and copolymers are certain Carbopol(R)-type, cross-linked carboxyvinyl polymers such as Carbopol(R)-940 ex B.F. Goodrich Co Ltd. Other examples are the Viscalex products ex Allied Colloids, which are emulsions of (meth)acrylic acid copolymers with (meth)acrylate esters, e.g. Viscalex HV 30, Acrysols (ex Rohm & Haas) and Ubatols (ex Stapol).

Examples of appropriate mixtures of such thickening agents are mixtures of Shellflo-XA with PPE 1042, Shellflo-XA with Carbopol 940, and Shellflo-XA with Viscalex HV30.

Both the gum-type and the acrylic copolymer-type thickening agents have been described in our European Patent Application 0 174 689, published on 19 March 1986, in which representatives of both types have been described for inclusion in shear-thinning liquid cleaning compositions. This publication is hereby incorporated by way of Reference.

The linear non-starch type polymer can include synthetic polymers such as those having an average molecular weight of more than 50,000, preferably more than 500,000 up to a preferred upper limit of about 10,000,000. Examples of such linear synthetic polymers include polyvinylalcohol, polyacrylate and polyvinylpyrrolidone. Alternatively the linear non-starch type polymer can be derived from natural sources and is suitably a gum-type

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polymer. Gums, or micilages as they are sometimes called, basically consist of a variety of polysaccharides with varying polymerisation degrees. Unlike starch any one gum can contain a variety of saccharide units, e.g. glucose, manose, fructose, galactose and each saccharide unit is linked to its neighbour by a (1) \rightarrow (4) beta glucoside linkage. Gums are very high molecular weight polymers and normally have a molecular weight between 1,000,000 and 2,000,000. Examples of suitable gum-type thickening agents are as given above.

By "branched starch type polymer" is meant a starch type polymer in which at least 70% of constituent molecules are branched. Preferably at least 85% of molecules comprising the branched starch type polymer are branched. Cross linking may additionally be present. The molecular weight of the branched starch type polymer is preferably more than 1,000,000 and can be up to 2,000,000. Such materials are available commercially. More than one material can be present contributing to the branched starch type polymer. Starch type polymers are derived from natural plant sources such as maize, tapioca and potatoes. By "starch" is meant a polysaccharide consisting of D-glucose units having (1) \rightarrow (4) alpha glucosidic linkages in linear molecules and additionally (1) \rightarrow (6) alpha glucosidic linkages in branched molecules.

It is possible to alter the variables of a given system so as to manipulate otherwise unsuitable polymers into the A region or B (lower) region of their sigmoid curve and obtain the synergistic benefit. For example a mixture of 0.1% Shellflo XA (Figure 4) with 0.04% Carbopol 940 (Figure 5) in aqueous dispersion at pH 9.5 gives a synergistic increment of approximately 140% at 25°C, Figures 4 and 5 being respectively $\log \eta$ vs $\log c$ plots in

aqueous media at pH 9 to 10 for Shellflo XA and Carbopol 940. Alternatively a mixture of 0.1% Shellflo XA with 0.2% Carbopol 910 in aqueous dispersion at pH 9.5 gives a synergistic increment of approximately -30%. The Carbopol 940 therefore gives the synergistic benefit when mixed with Shellflo XA while Carbopol 910 does not for this particular system. It is believed that the explanation for this difference in behaviour lies in the observation that at 0.2% concentration Carbopol 910 is in the C region of its sigmoid curve for this system. Figure 6 is a plot of $\log \eta$ vs $\log c$ for Carbopol 910 in aqueous medium at pH 9 to 10. It follows that if A or B (lower) region behaviour could be induced in the Carbopol 910 by changing the system then the synergistic benefit would be obtained. The addition of 3% salt to a 0.1% Shellflo XA/0.2% Carbopol 910 mixture achieves this and a synergistic increment of 95% is seen. These results are given in Figure 7 which are plots of synergy in % vs concentration of Carbopol 910 in % for a 0.1% Shellflo XA solution with and without 3% NaCl.

For a particular system the synergistic increment can be calculated according to the equation given below

$$S = \left\{ \frac{\eta(P_1 + P_2) - 1}{\eta_{P_1} + \eta_{P_2}} - 1 \right\} \times 100$$

where S = the synergistic increment

$\eta(P_1 + P_2)$ = the viscosity of a mixture of polymers P_1 and P_2

η_{P_1} = the viscosity of polymer P_1

η_{P_2} = the viscosity of polymer P_2

Preferably the thickening mixture imparts a synergistic increment S of at least 5%, more preferably a

synergistic increment of at least 10%, even more preferably a synergistic increment of at least 50%.

Preparation

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10

Compositions of this invention can be prepared by mixing the various ingredients into water in a mixer. A suitable type of mixer is, for example, a turbine-stirred pot. The order of addition is unimportant, except that any polymeric thickener will generally be added last.

Packaging

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Compositions of this invention are, desirably, packed into dispensing containers which can include a manually operable dispensing pump which discharges the composition from a nozzle as an airless spray. Such a container, holding from 0.1 to 1 litre, preferably 0.2 to 0.6 litre, can be hand-held and used to spray the composition at a surface to be cleaned. Suitable spray dispensing pumps include the model 5910BA available from Afa-Polytek BV, Someren, Netherlands, and similar pumps marketed by Sundt-Semar, Canyon and Spraysol. Such pumps can be fitted to plastic bottles with a screw-threaded neck, e.g. a 500ml polyethylene bottle available from Bell Products Ltd, Wrexham, England.

Embodiments of the Invention

30

The invention will now be exemplified. In the following Examples all percentages are by weight of the whole composition unless otherwise stated.

35

Example 1

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A sprayable composition was prepared with the following formulation.

	<u>% by weight</u>
5	
Calcite	30
Sodium sesquicarbonate	1
Iso paraffin	
(boiling range 180-190°C)	15
10 Nonionic surfactant	
(C ₁₁₋₁₅ secondary alcohol 12 EO;	
boiling range >250°C)	0.5
Xanthan gum	0.1
Perfume	0.3
15 Water	balance to 100%

The calcite used had a specific surface area of $3\text{m}^2/\text{g}$ and a particle size in the range 0.5 to 12μ , average 2.8μ . 95% of particles were less than 10μ in size.

It can be seen that there was 90m^2 of calcite surface area per gram of sesquicarbonate (the only soluble electrolyte present), 180m^2 of calcite surface area per gram of surfactant, and 138m^2 of calcite surface area per gram of involatiles (taken to be the surfactant plus half the perfume).

The compositions had good suspending properties. Its viscosity was measured at a low shear rate of 10^{-1} sec^{-1} and at a high shear rate of 10^3 sec^{-1} . The former is an indicator of stability, cling to vertical surfaces and visual creaminess. The latter is an indicator of sprayability and spreadability. The measured values were 20000 cp at 10^{-1} and 55 cp at 10^3 sec^{-1} . This shows the composition to be strongly shear thinning.

Example 2

A sprayable composition was prepared with the following formulation.

5

	<u>% by weight</u>
Calcite	15
Sodium sesquicarbonate	1
10 Iso paraffin	
(boiling range 180-190°C)	14
Nonionic surfactant	
(C ₉₋₁₁ primary alcohol 6 EO;	
boiling point >250°C)	1
15 Xanthan gum	0.1
Perfume	0.3
Water	balance to 100%

20

The calcite used had a specific surface area of 6m²/g and an average particle size of 1.2μ. No particles exceeded 10μ in size.

25

It can be seen that there was 90m² of calcite surface area per gram of sesquicarbonate (the only soluble electrolyte present), 90m² of calcite surface area per gram of involatiles (taken as surfactant and half the perfume).

30

The composition had good suspending properties but was strongly shear thinning, with a viscosity of 10,000 cp at 10⁻¹ sec⁻¹ and 25 cp at 1000 sec⁻¹ shear rate.

Example 3

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- 23 -

A sprayable composition was prepared with the following formulation.

	<u>% by weight</u>
5	
Calcite	7.5
Sodium sesquicarbonate	0.3
Isopropanol	5.0
Nonionic surfactant	
10 (C ₉₋₁₁ primary alcohol 6 EO; boiling point >250°C)	0.5
Xanthan gum	0.2
Perfume	0.2
15 Water	balance to 100%

The calcite used had a specific surface area of $6\text{m}^2/\text{g}$ and an average particle size of 0.8μ . No particles exceeded 10μ in size.

20 It can be seen that there was 150m^2 of calcite surface area per gram of sesquicarbonate (the only soluble electrolyte present), 90m^2 of calcite surface area per gram of surfactant, and 75m^2 of calcite surface area per
25 gram of involatiles (taken as surfactant and half the perfume).

The composition had good suspending properties but was strongly shear thinning, with a viscosity of 2700 cp at 10^{-1} sec^{-1} and 11 cp at 1000 sec^{-1} shear rate.
30

Example 4

35 A series of compositions employing a variety of insoluble solids, with surfactant at various levels, were prepared and their effect in use was assessed. Each

- 24 -

composition contained 5% by weight of the insoluble solid, together with surfactant used in Examples 2 and 3 above, with the exception of two sets of compositions which used either sodium C₁₂ alkyl benzene sulphonate or the sodium salt of an alkyl ether sulphate (sulphated C₁₂-C₁₃ alcohol 3EO). Results with both anionics were essentially similar.

0.5ml of each composition was wiped over a glass mirror surface, 15 x 30cm, using a small piece (15 x 12cm) of dry, folded (3 times) perforated non-woven viscose cleaning cloth (J-cloth ex Johnson & Johnson). The film was left to dry, then the residue on the mirror surface was polished with a similar piece of cloth, dried and similarly folded. Polishing continued until all visible powder deposits removed.

The mirror was then viewed by a panel of people under single source intense lighting conditions (simulating car headlamps through windscreen or sun through window) for greasy smears radiating from image of light source. Rated as

- i) visible,
- ii) very slight, or
- iii) invisible.

Results are given in Table I below.

TABLE I

INSOLUBLE SOLID			SURFACTANT		SOLID TO SURFACTANT	
Nature	Average Particle Size (μ)	Specific Surface Area (sq m/g)	Nonionic % (w/w)	Ratio g/g	Ratio Solid SA/g of Surfactant	
10	0.8	5.5	i 0.7	7	39	
			ii 0.5	10	55	
			iii 0.4	12.5	69	
15	2.8	3.0	i 0.4	12.5	37	
			ii 0.2	25	75	
			iii 0.1	50	150	
20	1.2	6.0	i 0.6	8	48	
			ii 0.4	12.5	75	
			iii 0.3	17	102	
	2.1	5.5	i 0.6	8	46	
			ii 0.3	17	92	
			iii 0.2	25	137	

5	INSOLUBLE SOLID		SURFACTANT		SOLID TO SURFACTANT	
	Nature	Average Particle Size (μ)	Specific Surface Area (sq m/g)	Nonionic % (w/w)	Ratio g/g	Ratio Solid SA/g of Surfactant
10	Kaolin	7 (plates)	5.0	i 0.6	8	40
				ii 0.4	12.5	63
				iii 0.2	25	125
15	Dolomite	2.4	3.4	i 0.4	12.5	43
				ii 0.2	25	85
				iii 0.1	50	170
20	Calcite	2.8	3.0	Anionic % (w/w)		
				i 0.9	5.5	16
				ii 0.7	7	21
25				iii 0.6	8	24

It can be seen from Table I that visible streaking was observed when the ratio of solid surface area/weight of surfactant was below $50\text{m}^2/\text{gram}$.

5 Examples 5 to 7

Three sprayable compositions were prepared with the following formulations:

10	<u>Example</u>	<u>5</u>	<u>6</u>	<u>7</u>	
	Calcite	10.0	20.0	35.0	(wt%)
	Nonionic surfactant	0.1	0.5	0.5	(wt%)
	(Dobanol 91-5T)				
15	Solvent Isopar L	3.0	0.0	10.0	(wt%)
	n-PGMBE	0.0	1.5	0.0	(wt%)
	Shellflo XA	0.2	0.2	0.2	(wt%)
	PPE 1042	0.5	0.5	0.5	(wt%)
	Perfume	0.3	0.3	0.3	(wt%)
20	Preservative	0.05	0.05	0.02	(wt%)
	Water	to 100	to 100	to 100	(wt%)

25 The calcite used had a specific surface area of $2\text{m}^2\text{g}^{-1}$. and an average particle size of $5\mu\text{m}$. No particles exceeded $25\mu\text{m}$ in size.

30 Shellflo XA, also known as Maxaflo, is a xanthan gum thickening agent available from Shell Chemicals Ltd. PPE 1042 is a cross-linked acrylic copolymer sold by National Starch and Chemical Ltd.

The pH of each composition was adjusted as necessary with NaOH to 9.5.

The ratio of surface area of insoluble solid (ie. calcit) to weight involatile liquids was thus 80:1 for Example 5, 60:1 for Example 6 and 108:1 for Example 7.

Each of Examples 5 to 7 were tested using the mirror test described under Example 4 and each was rated invisible i.e. no streaks or smears. A similar cleaning test for each composition applied to a solid blue textured surface yielded a surface showing no residues.

Examples 8 to 23

A series of experiments was carried out to illustrate the influence of the boiling point of the solvent, and hence the overall quantity of defined involatiles present, in a variety of formulations.

Sixteen samples were prepared contained in two sets incorporating a variety of eight different solvents at levels of 0.2 wt% and 5.0 wt% respectively. The solvents employed had a variety of boiling points as follows:

3 paraffins (water insoluble):

	B pt Range (°C)	Evaporation Rate
Isopar G	155-173	0.28
Isopar L	188-206	0.04
Isopar M	204-254	<0.01

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5 glycol ethers (water soluble)

	B pt (°C)	Evaporation Rate
5 Dowanol PnB	170	0.07
Dowanol DPnB	230	0.01
Hexyl Carbitol	259	<0.01
Butyl Cellusolve	170	0.08
Butyl Digol	230	0.004

10 Each of Isopar G, Isopar L and Isopar M is a branched paraffin of industrial grade and is water insoluble.

15 Dowanol PnB is a propylene glycol monobutyl ether.
Dowanol DPnB is a dipropylene glycol monobutyl ether.
Hexyl Carbitol is diethylene glycol monohexyl ether.
Butyl cellusolve is 2-butyoxyethanol. Butyl digol is diethylene glycol monobutyl ether. Each of these five materials is a water soluble glycol ether.

20 Each of these solvents was included in the following base formulation:

	wt%
25 Calcite (Durcal 5)	35
Polyacrylate polymer (PPE 1042)	0.5
Polysaccharide polymer (Maxaflo)	0.2
Nonionic surfactant (Dobanol 91-5T)	0.5
30 Anionic surfactant (Coco PAS)	0.5
Perfume	0.3
Preservative	0.05
NaOH	to pH 10.5
Water	to 95wt%

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- 30 -

In one set each solvent was present at a level of 5wt% with respect to the total composition. In the other set the solvent was present at a level of 0.2wt%, the balance to 100wt% being water.

5

In each case the formulation contained 35wt% of a calcite abrasive known as Durcal 5 which had a surface area of 68.25m^2 per 35g calcite (approximately equal to $2\text{m}^2/\text{g}$). Involatiles in each formulation were constituted by the nonionic and the anionic surfactant, by 50% of the perfume present and when present by Isopar M, Dowanol DPnB, butyl digol and hexyl carbitol. Table II below gives the total amount of involatiles in each 100g of each formulation and the ratio of the calcite surface area to the total weight of involatiles present.

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- 31 -

Table II

<u>Example</u>	<u>Solvent</u>	<u>Total</u> <u>Involatiles (g)</u>	<u>Ratio</u> <u>(m²/g:g)</u>
5			
8	0.2wt% PnB	1.15	59.4:1
9	5.0wt% PnB	1.15	59.4:1
10	0.2wt% DPnB	1.35	50.5:1
11	5.0wt% DPnB	6.15	11.1:1
12	0.2wt% HexC	1.35	50.5:1
13	5.0wt% HexC	6.15	11.1:1
14	0.2wt% Butyl cellusolve	1.15	59.4:1
15	5.0wt% Butyl cellusolve	1.15	59.4:1
16	0.2wt% Butyl digol	1.35	50.5:1
17	5.0wt% Butyl digol	6.15	11.1:1
18	0.2wt% Isopar G	1.15	59.4:1
19	5.0wt% Isopar G	1.15	59.4:1
20	0.2wt% Isopar L	1.15	59.4:1
21	5.0wt% Isopar L	1.15	59.4:1
22	0.2wt% Isopar M	1.35	50.5:1
23	5.0wt% Isopar M	6.15	11.1:1

Each of the formulations of Examples 8 to 23 was employed in the mirror test described under Example 4. The results in the present instance were scored according to the following five point scale:

30	1	=	no streaks/smears
	2	=	very few streaks/smears
	3	=	some streaks/smears
	4	=	> 50% streaks/smears
35	5	=	completely covered

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The results are given in Table III below.

Table III

5	<u>Example</u>	<u>Calcite:Involatiles</u> <u>ratio (m²/g:g)</u>	<u>Mirror test score</u>
	8	59.4:1	1
	9	59.4:1	1
10	10	50.5:1	2
	11	11.1:1	4
	12	50.5:1	2
	13	11.1:1	4-5
	14	59.4:1	1
15	15	59.4:1	1
	16	50.5:1	2
	17	11.1:1	4
	18	59.4:1	1
20	19	59.4:1	1
	20	59.4:1	1
	21	59.4:1	1
	22	50.5:1	2
	23	11.1:1	4

25

30

The results in Table III illustrate the effect of employing in the formulation amounts of involatiles above and below the ratio of 50m²/g calcite per g involatiles. At ratios below the limit, i.e. formulations containing excess amount of involatiles, the results recorded were unacceptable comprising at least 50% streaks/smears. At ratios above the limit, i.e. formulations containing acceptable amounts of involatiles, the results recorded were acceptable, and improved as the ratio increased.

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CLAIMS

1. A liquid cleaning composition characterised in that it comprises 3 to 50wt% of a water-insoluble solid having an average particle size not greater than 100μ , suspended in an aqueous solution or emulsion comprising 30 to 90wt% water and 0.05 to 5wt% surfactant, with all percentages being based on the whole composition, characterised in that the ratio of the specific surface area of insoluble solid to the weight of those constituents of the composition which are involatile liquid and semi-liquids which do not boil at temperatures less than 220°C is at least 50 and not greater than 200 square metres per gram of these involatiles.
2. A composition according to claim 1 wherein the said ratio is in the range from 50 to 150 square metres per gram.
3. A composition according to claim 1 or claim 2 wherein the ratio of the specific surface area of the insoluble solid to the weight of soluble electrolyte (if any) in the composition is such that the insoluble solid provides at least 40 square metres of surface area per gram of dissolved electrolyte.
4. A composition according to claim 1 containing 0.01 to 3.5% by weight of an ~~at least~~ water dispersible polymeric thickener.
5. A composition according to claim 4 wherein the thickener is xanthan gum.
6. A composition according to claim 4 wherein the thickener comprises a thickening mixture comprising either

a gum-type polymer and an acrylic-type polymer or a linear non-starch type polymer and a branched starch type polymer, wherein each of the said polymers is selected according to its respective sigmoid curve of log
5 (viscosity) vs log (concentration) for the said composition, each polymer being selected from its sigmoid curve's lower portion having an increasing or substantially constant gradient, the composition having a viscosity of at least 20 cPs at a shear rate of 10 sec^{-1}
10 greater than that of the liquid cleaning composition in the absence of the said thickening mixture.

7. A composition according to claim 1 containing 0.2 to
15 20wt% of an organic solvent with a boiling point not over 220°C .

8. A composition according to claim 7 wherein the
20 solvent is water-insoluble and is selected from paraffinic and olefinic hydrocarbons boiling in the range 170 to 220°C and alkyl benzenes boiling in the range $150\text{--}190^{\circ}\text{C}$.

9. A composition according to claim 7 wherein the
25 solvent is at least partially water-soluble and is selected from C_2 to C_6 aliphatic alcohols and C_2 to C_4 glycol monoethers with C_2 to C_6 aliphatic alcohols.

10. A composition according to claim 1 wherein at least
30 ^{50 wt%} half the surfactant is nonionic.

11. A composition according to claim 1 wherein the amount
of insoluble solid is from 10 to 40% by weight based on the whole composition.

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12. A composition according to claim 1 including from 0.05 to 2.5% by weight of water-soluble carbonate, bicarbonate or sesquicarbonate.

5 13. A composition according to claim 1 wherein the said insoluble solid in the composition comprises particles having an average particle size less than 10μ with a specific surface area in the range from 1 to $7m^2$ per gram.

10 14. A composition according to claim 13 wherein the said insoluble solid also comprises particles having an average particle size from 15 to 100μ in a quantity from 1 to 20wt% based on the whole composition.

15 15. A composition according to claim 1 packed in a portable container provided with a pump for discharging the composition from the container as a spray.

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- 1 / 4 -

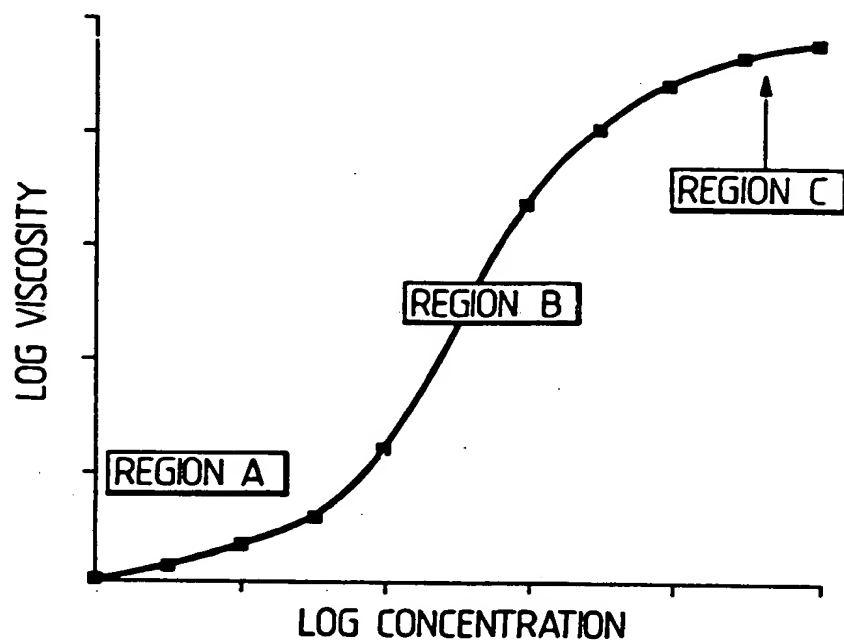
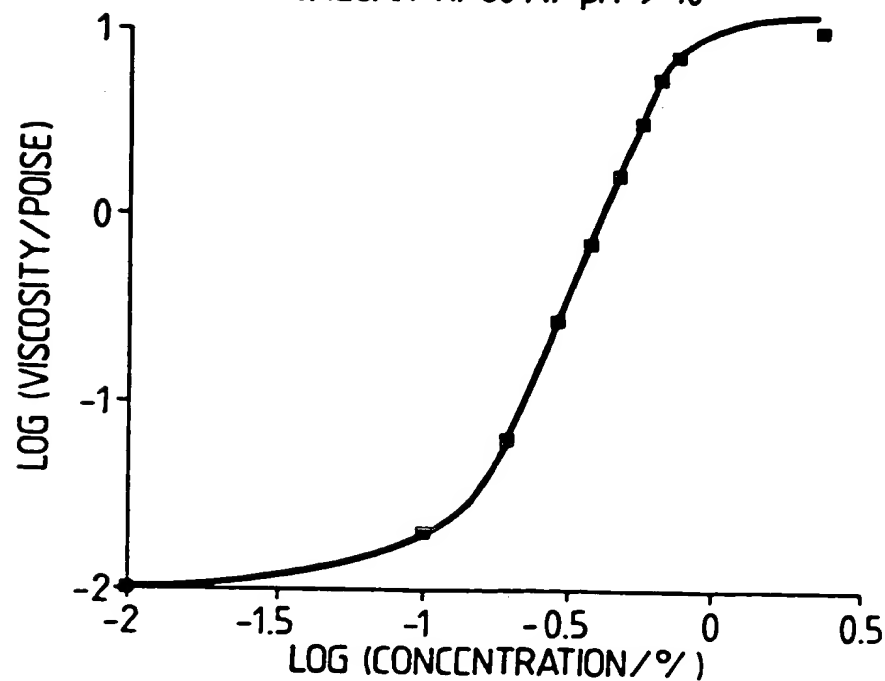
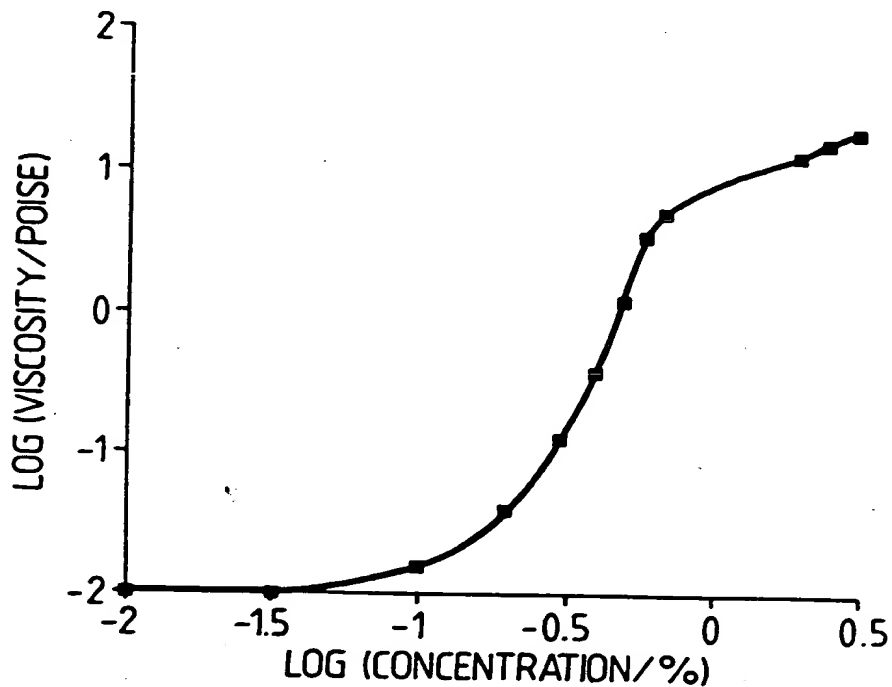
*Fig.1.*TYPICAL LOG VISCOSITY VS LOG CONCENTRATION PLOT
FOR AN AQUEOUS POLYMER SOLUTION*Fig.2.*TYPICAL SIGMOID CURVE FOR A GUM-TYPE POLYMER
JAGUAR HP60 AT pH 9-10

Fig.3

TYPICAL SIGMOID CURVE FOR A CROSS-LINKED POLYACRYLATE:
PPE 1042 AT pH 9-10

*Fig.4.*

LOG VISCOSITY VS LOG CONCENTRATION
FOR SHELLFLO XA AT pH 9-10

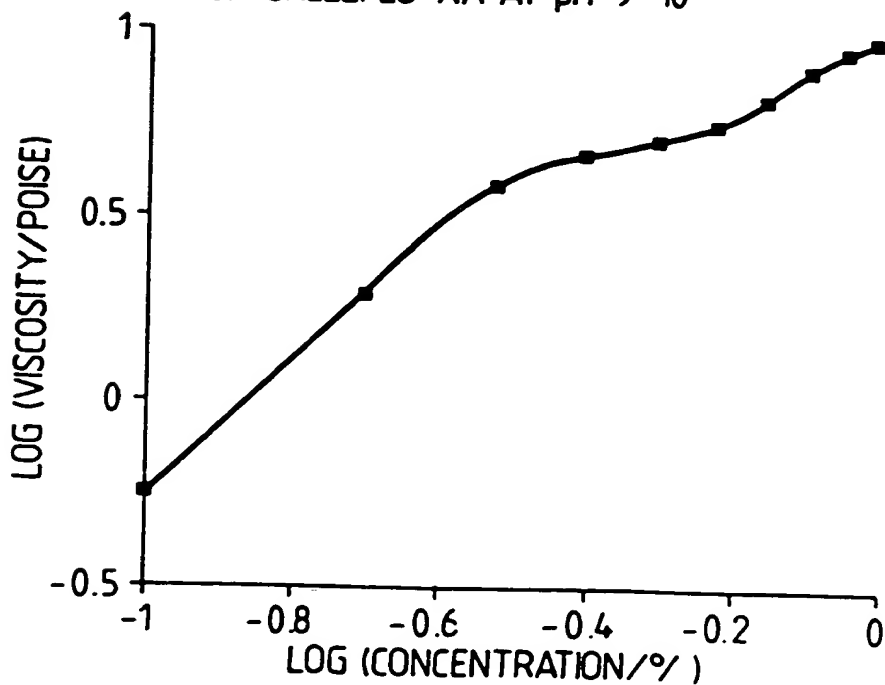
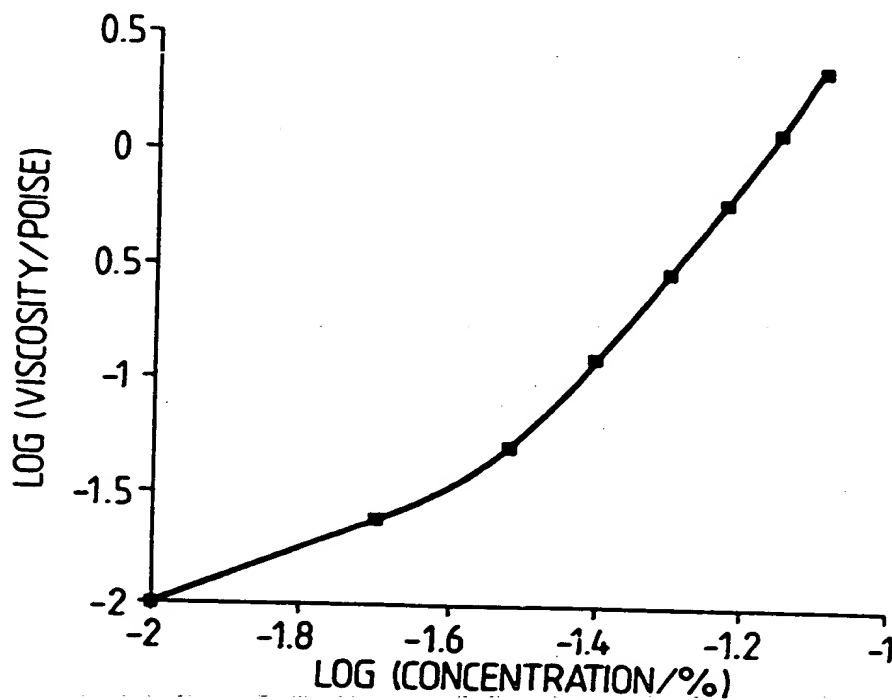
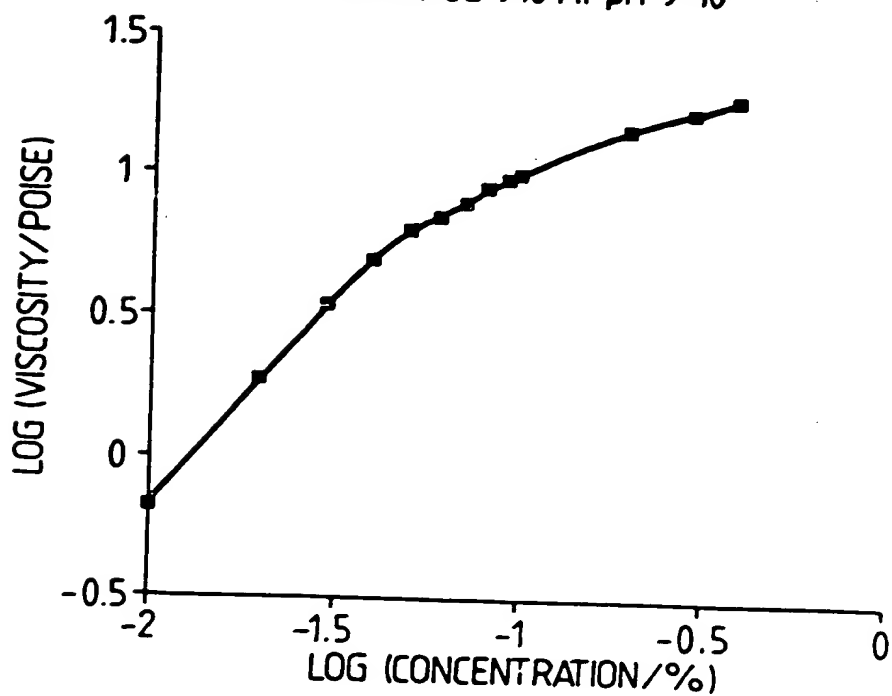


Fig.5.

LOG VISCOSITY VS LOG CONCENTRATION
FOR CARBOPOL 940 AT pH 9-10

*Fig.6.*

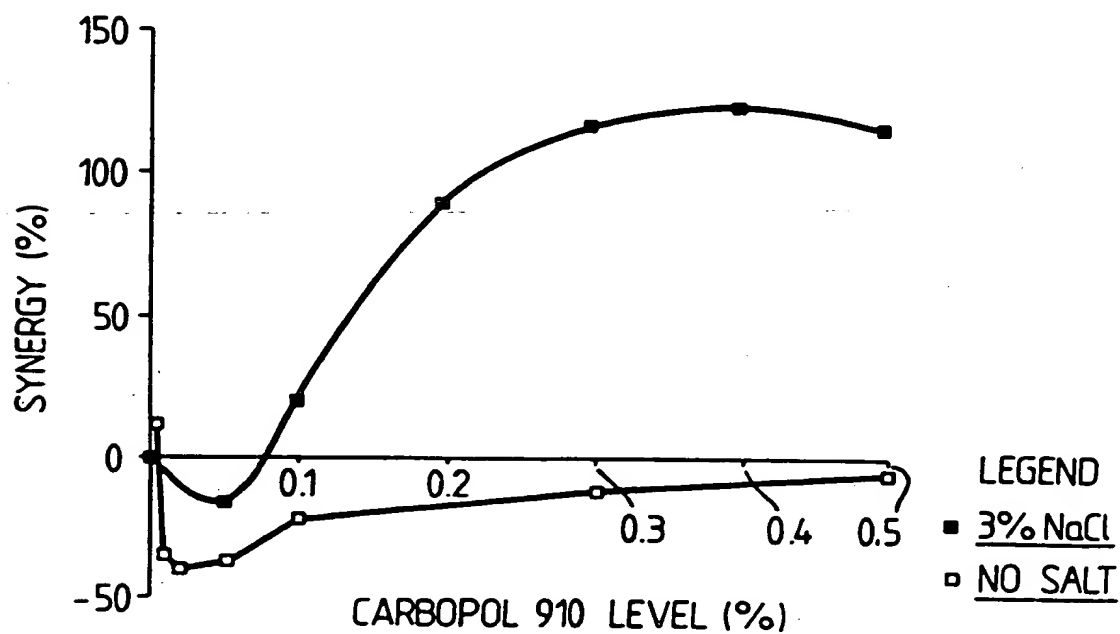
LOG VISCOSITY VS LOG CONCENTRATION
FOR CARBOPOL 910 AT pH 9-10



- 4 / 4 -

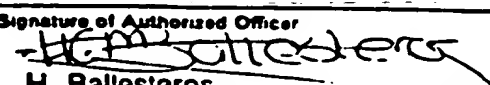
Fig.7.

VARIATION IN SYNERGY WITH CARBOPOL 910 LEVEL
FOR A 0.1% SHELLFLO XA SOLUTION IN THE PRESENCE/ABSENCE OF NaCl



INTERNATIONAL SEARCH REPORT

International Application No. PCT/GB 90/00549

I. CLASSIFICATION & SUBJECT MATTER (If several classification symbols apply, indicate all) According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 11 D 17/00, C 11 D 3/14, C 11 D 3/43																				
II. FIELDS SEARCHED <div style="text-align: center;">Minimum Documentation Searched *</div> Classification System: _____ Classification Symbols: _____ IPC ⁵ C 11 D																				
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *																				
III. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category *</th> <th style="width: 60%;">Citation of Document, ** with indication, where appropriate, of the relevant passages **</th> <th style="width: 30%;">Relevant to Claim No. **</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">Y</td> <td>EP, A, 0126545 (PROCTER & GAMBLE) 28 November 1984 see page 4, line 33 - page 7, line 33; examples and claims --</td> <td style="text-align: center;">1-12</td> </tr> <tr> <td style="text-align: center;">Y</td> <td>EP, A, 0214678 (PROCTER & GAMBLE) 18 March 1987 see the whole document --</td> <td style="text-align: center;">1-12</td> </tr> <tr> <td style="text-align: center;">Y</td> <td>EP, A, 0216416 (PROCTER & GAMBLE) 1 April 1987 see page 5, lines 5-37; examples and claims --</td> <td style="text-align: center;">1-12</td> </tr> <tr> <td style="text-align: center;">Y</td> <td>EP, A, 0226723 (VORWERK & CO.) 1 July 1987 see the claims --</td> <td style="text-align: center;">1-12</td> </tr> <tr> <td colspan="2" style="text-align: right;">./.</td> <td></td> </tr> </tbody> </table>			Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages **	Relevant to Claim No. **	Y	EP, A, 0126545 (PROCTER & GAMBLE) 28 November 1984 see page 4, line 33 - page 7, line 33; examples and claims --	1-12	Y	EP, A, 0214678 (PROCTER & GAMBLE) 18 March 1987 see the whole document --	1-12	Y	EP, A, 0216416 (PROCTER & GAMBLE) 1 April 1987 see page 5, lines 5-37; examples and claims --	1-12	Y	EP, A, 0226723 (VORWERK & CO.) 1 July 1987 see the claims --	1-12	./.		
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Y	EP, A, 0226723 (VORWERK & CO.) 1 July 1987 see the claims --	1-12																		
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: **</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Z" document member of the same patent family</p> </div> </div>																				
IV. CERTIFICATE																				
Date of the Actual Completion of the International Search 16th July 1990		Date of Mailing of this International Search Report 17. 08. 90																		
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer  H. Ballesteros																		

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	US, A, 4347151 (R.H. LOHR) 31 August 1982 see the examples and claims -----	1-12